

Superconductivity at 38 K in Iron-Based Compound with Platinum-Arsenide Layers $\text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$

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We report superconductivity in novel iron-based compounds $\text{Ca}_{10}(\text{Pt}_n\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ with $n = 3$ and 4. Both compounds crystallize in triclinic structures (space group $P\bar{1}$), in which Fe_2As_2 layers alternate with Pt_nAs_8 spacer layers. Superconductivity with a transition temperature of 38 K is observed in the $n = 4$ compound with a Pt content of $x \simeq 0.36$ in the Fe_2As_2 layers. The compound with $n = 3$ exhibits superconductivity at 13 K.

KEYWORDS: Iron-based superconductors, Ca-Fe-Pt-As

A number of iron-based superconductors have been identified since the discovery of superconductivity with a transition temperature (T_c) of 26 K in the fluorine-doped iron oxypnictide $\text{LaFeAsO}_{1-x}\text{F}_x$.¹⁾ All materials identified so far consist of alternating two-dimensional Fe_2As_2 layers and “spacer layers”. The central issues in realizing higher T_c are to seek novel spacer layers and engineer them to tune the electronic states of Fe_2As_2 layers in which high- T_c superconductivity emerges. The crystal structure of iron-based superconductors can be classified according to their spacer layers, which are (i) alkali or alkali-earth ions, as in LiFeAs ²⁾ and BaFe_2As_2 ,³⁾ (ii) slabs of rare-earth oxides or alkali-earth fluorides with a fluorite-type structure, as in LaFeAsO ¹⁾ and

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CaFeAsF ,⁴⁾ and (iii) complex metal oxides with perovskite-type structure or combinations of perovskite-type and rocksalt-type structures, as in $\text{Sr}_3\text{Sc}_2\text{O}_5\text{Fe}_2\text{As}_2$,⁵⁾ $\text{Sr}_4(\text{Sc}, \text{Ti})_3\text{O}_8\text{Fe}_2\text{As}_2$,⁶⁾ $\text{Sr}_4\text{V}_2\text{O}_6\text{Fe}_2\text{As}_2$,⁷⁾ $\text{Ca}_4(\text{Al}, \text{Ti})_2\text{O}_6\text{Fe}_2\text{As}_2$,^{8,9)} and their homologous series compounds.^{6,10–13)} All of these spacer layers consist of ionic chemical bonds, thus the spacer layers are insulating in nature.

In this letter, we report the discovery of novel iron-based superconductors with spacer layers made of covalent Pt arsenides. Using X-ray diffraction and chemical analyses, we identified the compounds to be $\text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ (referred to as α -phase) and $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ (referred to as β -phase). Both compounds crystallize in triclinic structures with the space group $P\bar{1}$ ($\# 2$). The α -phase exhibits superconductivity at $T_c \simeq 38$ K, the β -phase at $T_c \simeq 13$ K.

Single crystals of $\text{Ca}_{10}(\text{Pt}_n\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ were grown by heating a mixture of Ca, FeAs, Pt, and As powders. The mixture of 0.5 g with a ratio of Ca : Fe : Pt : As = 23 : 23 : 10 : 44 was placed in an alumina crucible (inner diameter of 6 mm and length of 60 mm) and sealed in an evacuated quartz tube. All manipulations were carried out in a glove box filled with argon gas. The ampules were heated in two ways. Heating at 700 °C for 3 h and then at 1000 °C for 72 h followed by slow cooling to room temperature yielded an α -phase with $T_c = 38$ K, whereas heating at 1100 °C and slow cooling to 1050 °C for 40 h yielded a β -phase with $T_c = 13$ K. The β -phase was obtained as a single phase without any secondary phases. In contrast, the α -phase was always obtained in the form of a mixture of α -phase crystals and slag containing nonsuperconducting $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$ ($x \simeq 0.08$) and Ca_2As powders. We obtained platelike crystals with a typical size of $1 \times 1 \times 0.1 \text{ mm}^3$ for both phases. The crystals were characterized by synchrotron radiation X-ray diffraction^{14,15)} and electron-probe microanalysis (EPMA). Longitudinal and Hall resistivities were measured using a Physical Property Measurement System (Quantum Design). Magnetization was measured using a SQUID magnetometer (Quantum Design).

Single-crystal structure analysis reveals that the compounds crystallize in triclinic structures with the space group $P\bar{1}$ ($\# 2$). The structures consist of alternating stacking of $(\text{Fe}_2\text{As}_2)_5$ and Pt_nAs_8 layers ($n = 4$ for α -phase and $n = 3$ for β -phase) with five Ca ions between them, as depicted in Figs. 1(a) and 1(b). Tiny crystals with dimensions of approximately $50 \times 50 \times 20 \text{ }\mu\text{m}^3$ prevented us from determining the superconducting and normal-state properties of the crystals used for single-crystal structure analysis. Thus we performed Rietveld refinement on the well-characterized samples

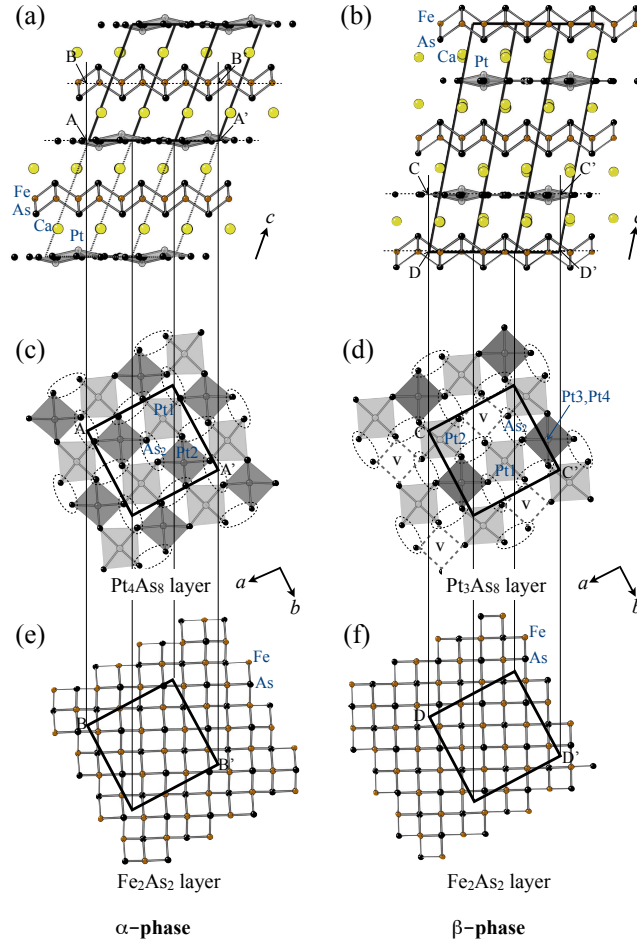


Fig. 1. (Color online) Crystal structures of $Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$ (α -phase) and $Ca_{10}(Pt_3As_8)(Fe_{2-x}Pt_xAs_2)_5$ (β -phase) with triclinic structures (space group $P\bar{1}$ (# 2)). Thick solid lines indicate the unit cell. (a), (c), and (e) show the schematic overviews of the α -phase, Pt_4As_8 layer, and $(Fe_2As_2)_5$ layer, respectively. The gray and dark-gray hatches in (c) indicate $PtAs_4$ squares with centric Pt1 and off-centered Pt2, respectively. The dashed ellipsoids in (c) represent As_2 dimers. (b), (d), and (f) show the schematic overviews of the β -phase, Pt_3As_8 layer, and Fe_2As_2 . The gray and dark-gray hatches in (d) indicate $PtAs_4$ squares with centric Pt1 and Pt2 and off-centered Pt3 and Pt4, respectively. The occupancy of Pt3 and Pt4 is ~ 0.5 . The dashed ellipsoids and 'v' in (d) represent As_2 dimers and Pt vacancies, respectively.

to clarify the relation of crystal structures and chemical compositions with superconducting and normal-state properties. The Rietveld refinement reveals the chemical compositions to be $Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$ with $x \simeq 0.36$ (α -phase) and $Ca_{10}(Pt_3As_8)(Fe_{2-x}Pt_xAs_2)_5$ with $x \simeq 0.16$ (β -phase). These chemical formulae yield atomic ratios of Ca : Fe : Pt : As = 23.8 : 19.5 : 13.8 : 42.9 for the α -phase and 24.4 : 22.4 : 9.3 : 43.9 for the β -phase, which are consistent with EPMA results: 22.9 : 23.9 :

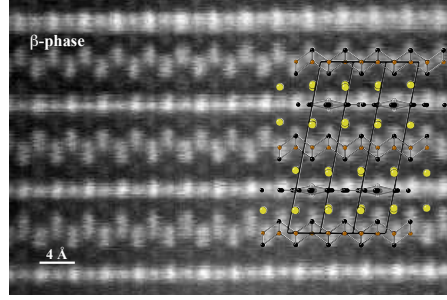


Fig. 2. (Color online) High-resolution TEM image of $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ (β -phase).

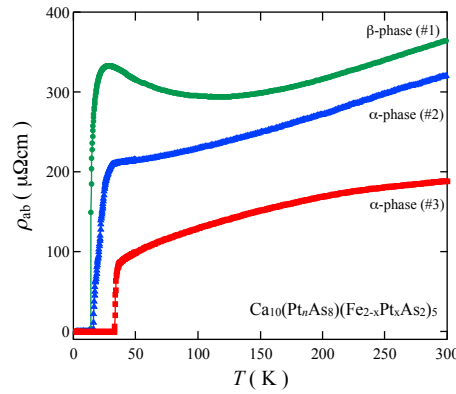


Fig. 3. (Color online) Temperature dependence of electrical resistivity for $\text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ (α -phase) and $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ (β -phase).

9.9 : 43.3 for the α -phase and 22.9 : 23.2 : 10.1 : 43.8 for the β -phase. Crystallographic data are summarized in Table I and II.

The most notable feature of the present compounds is the presence of Pt_nAs_8 layers, depicted in Figs. 1(c) and 1(d). These platinum arsenide layers are characterized by a distorted square lattice of corner-sharing PtAs_4 squares. Rotations of the PtAs_4 squares result in the formation of As_2 dimers, as indicated by the dashed ellipsoids in Figs. 1(c) and 1(d). Such As_2 dimers are observed in pyrite-type structures; the Pt_4As_8 layers can be derived from the ab -plane of pyrite PtAs_2 . The size of the Pt square lattice (with a Pt-Pt distance of approximately 4.4 Å) is by far larger than the size of the Fe_2As_2 square lattice (approximately 3.9 Å for CaFe_2As_2). This lattice mismatch leads to the formation of the $\sqrt{5} \times \sqrt{5}$ superstructure in the ab -plane in the present compounds, as depicted in Figs. 1(e) and 1(f). There exist Pt vacancies in the platinum arsenide layers of the β -phase, as shown in Fig. 1(d), to form the Pt_3As_8 layers.

The Pt_3As_8 layers alternating with Fe_2As_2 layers were directly confirmed for the

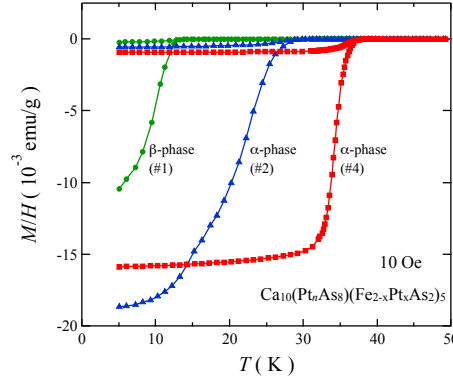


Fig. 4. (Color online) Temperature dependence of dc magnetization M measured in a magnetic field H of 10 Oe for $\text{Ca}_{10}(\text{Pt}_n\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ (α -phase) and $\text{Ca}_{10}(\text{Pt}_n\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ (β -phase).

β -phase, as shown in Fig. 2, by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEM-2100F, JEOL Co. Ltd.) with an aberration corrector (CEOS GmbH). In this image, intensity is approximately proportional to Z^2 , where Z is the atomic number; thus the brightest spots correspond to Pt, and the faintest spots correspond to Ca. Ca is located between the Fe_2As_2 and Pt_3As_8 layers, consistent with the X-ray refinements.

Figure 3 shows the electrical resistivity of α - and β -phases of different batches as a function of temperature. For sample #3 with the α -type structure, the resistivity shows metallic behavior. The resistivity starts to decrease sharply at 37 K and becomes negligibly small below 32.7 K. The 10%–90% transition width is approximately 2 K. This result suggests that the sample becomes superconducting below 32.7 K. The resistivity of #1 with the β -type structure exhibits semiconducting behavior below about 110 K, followed by a decrease below 27 K. Zero resistivity was observed below 13.5 K. The resistivity of #2 with the α -type structure shows an intermediate behavior between those observed in #1 and #3.

Evidence of bulk superconductivity can be seen in the temperature dependence of magnetization M shown in Fig. 4. All samples exhibited a diamagnetic behavior, a hallmark of superconductivity. The onset T_c 's were estimated to be 38 K, 29 K, and 13 K for #4, #2, and #1, respectively. The shielding volume fraction at 5 K without demagnetizing-field corrections were 139, 163, and 82% for #4, #2, and #1, respectively. Thus the highest T_c of 38 K was obtained in the α -phase (#4).

The Hall coefficient R_H , shown in Fig. 5, is negative for all samples, suggesting that the major carriers are electrons in both α - and β -phases. The strong temperature de-

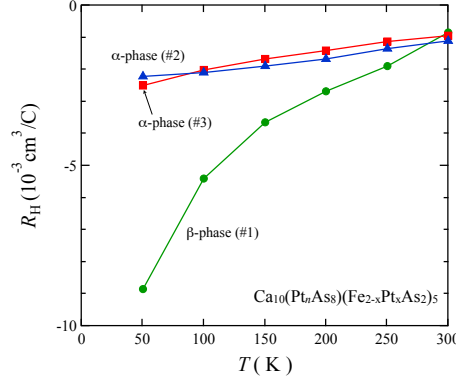


Fig. 5. (Color online) Temperature dependence of Hall coefficient for $\text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ (α -phase) and $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ (β -phase).

pendence of R_H observed in the β -phase (#1), as well as the semiconducting resistivity at low temperatures, is reminiscent of underdoped materials. Indeed, analogous behaviors are observed in the underdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ with $x = 0.05$.¹⁶⁾ R_H for the α -phase (#2 and 3) exhibits a weak but distinct temperature dependence, which again is analogous to those reported in optimally doped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ with $x = 0.09$.¹⁶⁾ The Pt content of $x/2 \simeq 0.18$ for optimally doped $\text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ is by far larger than the Co content for optimally doped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ ($x = 0.09$), suggesting that Pt causes the doping of fewer electrons than Co, the most studied dopant for iron-based materials. This is consistent with the absence of superconductivity in $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$ up to the solubility limit of $x \simeq 0.08$.

Formal electron counts of As_2 dimers and isolated As are $[\text{As}_2]^{4-}$ and As^{3-} , respectively. Since all As atoms form dimers in Pt_nAs_8 layers and all As atoms are isolated in Fe_2As_2 layers, we expect a formal electron count of Fe^{2+} and Pt^{2+} for the β -phase, $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5$. Thus, $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5$ can be viewed as a parent compound.

The novel spacer layers of the present materials, namely, Pt_nAs_8 ($n = 3$ and 4) layers, will give us a unique opportunity to further engineer iron-based materials to optimize superconductivity. First, the present materials with an interlayer distance between Fe_2As_2 of $d \simeq 10$ Å fill the materials gap between SmFeAsO with $d \simeq 8.6$ Å and $\text{Sr}_4\text{V}_2\text{O}_6\text{Fe}_2\text{As}_2$ with $d \simeq 15.67$ Å. Smaller d than that of SmFeAsO tends to lead to lower T_c .^{13,17)} Larger d than that of $\text{Sr}_4\text{V}_2\text{O}_6\text{Fe}_2\text{As}_2$ also seems to lead to lower T_c .¹³⁾ We naively expect that an optimal distance for higher T_c may exist in the d range of the present materials. Secondly, the nature of chemical bonds of the spacer layers

seems to be quite different between the present materials and the previous iron-based superconductors. The spacer layers of the previous materials, alkali/alkali-earth ions or complex oxides/fluorides, are electrically inert because of the ionic chemical bonds. Thus no atomic orbitals of the spacer layers mix with the Fe $3d$ orbitals of the superconducting Fe_2As_2 layers. In contrast, the chemical bonds of the present spacers layers, a platinum arsenide, are covalent in nature; thus we expect that Pt orbitals may contribute to charge transport and possibly to superconductivity. Indeed, most platinum arsenides are metallic and even superconductivity has been observed in SrPt_2As_2 ¹⁸⁾ and SrPtAs .¹⁹⁾ Further investigations will be invaluable to determine whether novel electronic states are realized in the present materials.

Recently, Ni *et al.*²⁰⁾ reported superconductivity and crystal structures on $\text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_2\text{As}_2)_5$ and $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5$, based on our previous report.²¹⁾ The α -phase and β -phase in the present study most likely correspond to 10-4-8 and 10-3-8 phases reported by Ni *et al.*²⁰⁾ Higher T_c was observed in the present study, likely due to the difference in Pt contents in the Fe_2As_2 layers.

In summary, we reported that the quaternary iron-based materials $\text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ and $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ exhibit superconductivity at 38 K and 13 K, respectively. Both materials consist of novel platinum-arsenide spacer layers, namely, Pt_nAs_8 layers. This finding demonstrated that a variety of spacer layers are possible in iron-based superconductors. Engineering of this novel spacer layer will lead to higher superconducting transition temperatures in this class of materials.

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Table I. Crystallographic parameters of α -phase. M site represents $\text{Fe}_{1-x/2}\text{Pt}_{x/2}$ with $x = 0.36(4)$. Chemical formula is $\text{Ca}_{10}\text{Fe}_{8.2}\text{Pt}_{4.8}\text{As}_{18}$. The occupancy is fixed at 1 in all atomic sites. $R_{wp} = 6.39\%$ and $RI = 7.67\%$.

The α -phase			
Triclinic with space group $P\bar{1}$ (# 2).			
$a = 8.719(1)$ Å, $b = 8.727(1)$ Å, $c = 11.161(1)$ Å.			
$\alpha = 99.04(2)^\circ$, $\beta = 108.21(2)^\circ$, $\gamma = 90.0(2)^\circ$.			
atomic positions			
site	x/a	y/b	z/c
Ca01	0.338(1)	0.2818(6)	0.2404(2)
Ca02	0.135(1)	0.6868(6)	0.2404(2)
Ca03	0.542(1)	0.8785(6)	0.2404(2)
Ca04	0.744(1)	0.4850(6)	0.2404(2)
Ca05	0.935(1)	0.0794(6)	0.2404(2)
M 01	0.645(2)	0.453(4)	0.500(1)
M 02	0.846(2)	0.053(4)	0.500(1)
M 03	0.246(2)	0.253(4)	0.500(1)
M 04	0.446(2)	0.853(4)	0.500(1)
M 05	0.044(2)	0.653(4)	0.500(1)
Pt01	0.750(2)	0.250(2)	0.000(1)
Pt02	0.234(1)	0.235(2)	0.9421(5)
As01	0.4854(6)	0.6155(9)	0.36805(7)
As02	0.2849(6)	0.0175(9)	0.36805(7)
As03	0.6842(6)	0.2167(9)	0.36805(7)
As04	0.0861(6)	0.4168(9)	0.36805(7)
As05	0.8857(6)	0.8171(9)	0.36805(7)
As06	0.848(3)	-0.496(3)	1.004(3)
As07	-0.345(3)	-0.025(3)	1.004(3)
As08	-0.005(3)	-0.142(3)	1.004(3)
As09	0.504(3)	-0.372(3)	1.004(3)

Table II. Crystallographic parameters of β -phase. M site represents $\text{Fe}_{1-x/2}\text{Pt}_{x/2}$ with $x = 0.16(1)$. Chemical formula is $\text{Ca}_{10}\text{Fe}_{9.20}\text{Pt}_{3.80}\text{As}_{18}$. The occupancy is fixed at 1 in all atomic sites except for Pt03 and Pt04. The occupancy is determined to be 0.447(3) at Pt03 and Pt04. $R_{wp} = 4.82\%$ and $RI = 7.77\%$.

The β -phase			
Triclinic with space group $P1$ ($\# 2$).			
$a = 8.795(3) \text{ \AA}$, $b = 8.789(3) \text{ \AA}$, $c = 21.008(7) \text{ \AA}$.			
$\alpha = 94.82(8)^\circ$, $\beta = 99.62(9)^\circ$, $\gamma = 89.99(3)^\circ$.			
atomic positions			
site	x/a	y/b	z/c
Ca01	0.0005(3)	1.1278(3)	0.3667(1)
Ca02	-0.2915(3)	1.4761(3)	1.1335(1)
Ca03	-0.1978(3)	1.2793(3)	0.6326(1)
Ca04	-0.3940(3)	1.6750(3)	0.6327(1)
Ca05	0.1976(3)	1.4779(3)	0.6330(1)
Ca06	-0.2997(3)	1.7221(3)	0.8674(1)
Ca07	0.0928(3)	0.9186(3)	0.8669(1)
Ca08	-0.5095(3)	1.1200(3)	0.8519(1)
Ca09	-0.1035(3)	1.3267(3)	0.8680(1)
Ca10	-0.5906(3)	1.0794(3)	0.6480(1)
M01	-0.1522(2)	0.5506(2)	0.9999(6)
M02	-0.0503(2)	0.8516(2)	1.0014(6)
M03	-0.2525(2)	0.2492(2)	0.9998(7)
M04	-0.3518(2)	0.9503(2)	0.9999(8)
M05	-0.4506(2)	0.6508(2)	0.9991(7)
M06	0.1497(2)	0.9501(2)	0.4992(7)
M07	-0.3514(2)	1.4492(2)	0.49866(6)
M08	-0.4501(2)	1.1490(2)	0.50007(7)
M09	0.2506(2)	1.2478(2)	0.5002(7)
M10	-0.0506(2)	1.3481(2)	0.50013(6)
Pt01	0.45028(6)	0.59961(5)	0.74990(2)
Pt02	-0.04976(6)	0.10073(5)	0.75011(2)
Pt03	-0.0389(1)	0.6055(1)	0.77790(4)
Pt04	-0.0615(1)	0.5943(1)	0.72210(4)
As01	0.2187(2)	0.9996(1)	0.75004(5)
As02	-0.4513(2)	0.8670(1)	0.75008(5)
As03	0.3249(2)	1.0356(2)	0.43135(6)
As04	-0.2920(2)	1.4827(2)	0.75010(7)
As05	-0.5236(2)	1.3607(2)	0.56856(6)
As06	-0.1245(2)	1.5642(2)	0.56678(6)
As07	-0.1813(2)	1.0362(2)	0.93135(7)
As08	0.0670(2)	1.3569(2)	0.74993(8)
As09	-0.3803(2)	1.4343(2)	0.93125(7)
As10	0.0237(2)	1.6376(2)	0.93316(7)
As11	0.0785(2)	1.1619(2)	0.56872(6)
As12	-0.2255(2)	1.7656(2)	1.06898(7)
As13	-0.1693(2)	0.8453(2)	0.74997(7)
As14	-0.2780(2)	1.2332(2)	0.43126(6)
As15	0.3500(2)	1.3384(1)	0.74993(6)
As16	-0.5776(2)	1.8381(2)	0.93099(7)
As17	0.1940(2)	0.7191(2)	0.74993(7)
As18	-0.3118(2)	1.1976(1)	0.75022(6)

References

- 1) Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono: J. Am. Chem. Soc. **130** (2008) 3296.
- 2) J. H. Tapp, Z. Tang, B. Lv, K. Sasmal, B. Lorenz, P. C. W. Chu, and A. M. Guloy: Phys. Rev. B **78** (2008) 060505(R).
- 3) M. Rotter, M. Tegel, and D. Johrendt: Phys. Rev. Lett. **101** (2008) 107006.
- 4) S. Matsuishi, Y. Inoue, T. Nomura, H. Yanagi, M. Hirano, and H. Hosono: J. Am. Chem. Soc. **130** (2008) 14428.
- 5) X. Zhu, F. Han, G. Mu, B. Zeng, P. Cheng, B. Shen, and H.-H. Wen: Phys. Rev. B **79** (2009) 024516.
- 6) N. Kawaguchi, H. Ogino, Y. Shimizu, K. Kishio, and J. Shimoyama: Appl. Phys. Express **3** (2010) 063102.
- 7) X. Zhu, F. Han, G. Mu, P. Cheng, B. Shen, B. Zeng, and H.-H. Wen: Phys. Rev. B **79** (2009) 220512(R).
- 8) H. Ogino, K. Machida, A. Yamamoto, K. Kishio, J. Shimoyama, T. Tohei, and Y. Ikuhara: Supercond. Sci. Technol. **23** (2010) 115005.
- 9) P. M. Shirage, K. Kihou, C.-H. Lee, H. Kito, H. Eisaki, and A. Iyo: Appl. Phys. Lett. **97** (2010) 172506.
- 10) H. Ogino, Y. Katsura, S. Horii, K. Kishio, and J. Shimoyama: Supercond. Sci. Technol. **22** (2009) 085001.
- 11) Y. Matsumura, H. Ogino, S. Horii, Y. Katsura, K. Kishio, and J. Shimoyama: Appl. Phys. Express **2** (2009) 063007.
- 12) S. Sato, H. Ogino, N. Kawaguchi, Y. Katsura, K. Kishio, J. Shimoyama, H. Kote-gawa, and H. Tou: Supercond. Sci. Technol. **23** (2010) 045001.
- 13) H. Ogino, S. Sato, K. Kishio, J. Shimoyama, T. Tohei, and Y. Ikuhara: Appl. Phys. Lett. **97** (2010) 072506.
- 14) E. Nishibori, M. Takata, K. Kato, M. Sakata, Y. Kubota, S. Aoyagi, Y. Kuroiwa, M. Yamakata, and N. Ikeda: Nucl. Instr. Meth. Phys. Res. A **467-468** (2001) 1045.
- 15) K. Sugimoto, H. Ohsumi, S. Aoyagi, E. Nishibori, C. Moriyoshi, Y. Kuroiwa, H. Sawa, and M. Takata: AIP Conf. Proc. **1234** (2010) 887.

- 16) N. Katayama, Y. Kiuchi, Y. Matsushita, and K. Ohgushi: J. Phys. Soc. Jpn. **78** (2009) 123702.
- 17) C.-H. Lee: Rev. High Pressure Sci. Technol. **19** (2009) 119 [in Japanese].
- 18) K. Kudo, Y. Nishikubo, and M. Nohara: J. Phys. Soc. Jpn. **79** (2010) 123710.
- 19) Y. Nishikubo, K. Kudo, and M. Nohara: J. Phys. Soc. Jpn. **80** (2011) 055002.
- 20) N. Ni, J. M. Allred, B. C. Chan, and R. J. Cava: arXiv:1106.2111.
- 21) M. Nohara, S. Kakiya, and K. Kudo: presented at International Workshop on Novel Superconductors and Super Materials 2011 (NS²2011), Tokyo, Japan, March 6-8, 2011.

Note added in proof – We noticed a paper by Löhnert *et al.* [arXiv: 1107.5320] reporting similar results with T_c up to 35 K, based on our previous report.²¹⁾